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PATENT ABSTRACTS OF JAPAN

(11) Publication number: **07085972 A**(43) Date of publication of application: **31.03.95**

(51) Int. Cl.

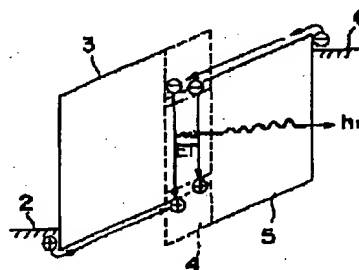
H05B 33/14**G09F 9/30****G09G 3/30****H01L 33/00**(21) Application number: **05233827**(22) Date of filing: **20.09.93**(71) Applicant: **TOSHIBA CORP**(72) Inventor:
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EKUSA TAKASHI
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SASAKI TAKASHI**(54) ORGANIC EL ELEMENT****(57) Abstract:**

PURPOSE: To enhance the light emitting efficiency and prolong the lifetime by forming an organic thin film from an electron implanting layer, hole implanting layer, recoupling region, and light emission site, and by locating this thin film between an electrode for electron implantation and an electrode for hole implantation.

CONSTITUTION: When a bias voltage is impressed so that an Mg-Ag electrode (electrode for electron implantation) 6 becomes negative while an ITO electrode (electrode for hole implantation) 2 becomes positive, each electron implanted from the electrode 6 are conveyed in an electron implantation layer 5 and farther through a recoupling layer 4, but does not reach a hole implantation layer 3. Holes implanted from the ITO electrode 2, on the other hand, are conveyed in the hole implantation layer 3 and farther through the recoupling layer 4, but do not reach the electron implantation layer 5. Exciplex of OXD-7/ diamine is produced in the recoupling layer 4, and an energy transition takes place into vis (phenylethynyl) anthracene as a light emissive molecule (light emitting site), and as a result light

emission occurs. Organic thin films of these layers 3, 4, 5 have amorphous structure.

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[0024] A luminescence site means the molecule or molecule pair which emits light in response to an energy transfer from the recombination site excited by the reunion of the electron and hole in a recombination field (a luminescence site may only be called luminescent molecule below). In order to judge whether a certain molecule serves as a luminescence site, it is effective to compare EL spectrum with the emission spectrum by optical pumping of the molecule, and if both are in agreement, it can be said that it is a luminescence site.

[0025] An energy transfer means the phenomenon which excitation energy moves to an acceptor from a donor according to the dipole-dipole interaction or multipole child interaction committed between the molecules or molecular assemblies (energy acceptor) in the molecule or molecular assembly (energy donor) in an excitation state, and other ground states. It works to a long distance comparatively and these interactions do not need the lap (lap of an electron cloud) of a donor and an acceptor. The travel is defined by the interaction radius R and, generally R is in the range of 10nm or less.

[0026] Voltage is impressed to inter-electrode [two], an electron and a hole are poured in into an organic thin film, a recombination site will be in an excitation state and the organic EL element concerning this invention operates by the mechanism in which the excitation energy carries out an energy transfer to a luminescence site, and emits light to it, when an electron and a hole recombine in a recombination field. If it puts in another way, the organic EL element of this invention will be the so-called functional discrete-type element to which the molecule which bears the process to reunion, and the molecule which bears the process of luminescence are separated, and an energy transfer intervenes among such 2 process. If learned and expressed to (1) formula which mentioned above the luminous efficiency of the organic EL element of such a functional discrete type, it will become like (2) formulas. Here, efficiency of the energy transfer from a recombination site to the luminescence site of an excitation state is set to etaephemeris time.

[0027] eta EL-eta inj xetarec xeta ephemeris timexeta PL — (2)

Since the organic EL element of this invention is a functional discrete type, it can be separated and considered also about the means which raises the efficiency of two process. Hereafter, in the organic EL element of this invention, how to raise the efficiency of each process is explained theoretically.

[0028] First, process [the process to reunion], i.e., (etainj xetarec), in order to make it improve, an electron and a hole are poured in efficiently to a recombination field (etainj is high), an electron and a hole exist with sufficient balance in the layer in which a recombination site exists, and what (etarec is high) an electron and a hole are conveyed to a recombination site and recombine efficiently is required. It means that these conditions show property with a recombination field sufficient in respect of both carrier injections and transportability.

[0029] Moreover, in order to raise the efficiency of the process of luminescence, it is required to raise efficiency etaephemeris time of an energy transfer and luminous efficiency etaPL of a luminescence site. Hereafter, how to raise etaPL is explained, taking etaephemeris time into consideration. Although that to which etaPL of an organic molecule exceeds 90% in an isolated state, i.e., a gaseous state, and the dilute solution is not new, either, if it is made an amorphous thin film, most will fall to less than 30%. The interaction of the adjoining molecule can be considered as a cause of this fall. It is so large that the energy level of the interaction of a molecule is near. That is, although the interaction of molecules of the same kind is large, it can be made small if it is the interaction of molecules of a different kind. Therefore, etaPL can be raised if it dopes so that a luminescent molecule may be in a false isolated state to a surrounding molecule. A luminescence site may be distributed as an isolated molecule and you may make it distribute as a microcrystal as the method of doping. When making it distribute as a microcrystal, in order to set the maximum droplet size to 10nm or less and to abolish an electric defect, it is desirable that a surrounding field is amorphous structure. In addition, as for the distance of a recombination site and a luminescence site, it is desirable that it is 10nm or less. This is because efficiency etaephemeris time of an energy transfer will decrease exponentially if the distance of a recombination site and a luminescence site becomes large. Moreover, as for the concentration of the luminescent molecule in within the limits of less than 10nm, it is desirable for the distance from the recombination field of the layer containing a luminescence site to be 0.5-5-mol%. Since the efficiency of the energy transfer from a recombination site to a low and a luminescence site falls [concentration] rather than this, etaephemeris time falls. Moreover, if concentration is higher than this, since a luminescence site cannot be isolated, etaPL will fall. Since etaEL proportional to this has the maximal value if it is the concentration of the above-mentioned range as a result (eta ephemeris timexeta PL), it is desirable.

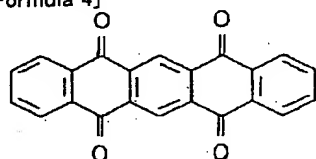
[0030] The concrete means for raising hereafter the luminous efficiency of the organic EL element adopted in this invention is explained more to a detail. First, the organic EL element of invention of this application 1st is explained. By constituting a recombination field from a molecule pair of an electron-injection nature child and a hole pouring nature child, this application the 1st invention raises the efficiency of both carrier injections, transportation, and reunion, by on the other hand doping a luminescent molecule, raises the luminous efficiency by optical pumping, and, on the whole, raises the luminous efficiency of an organic EL element. In this case, the clearly distinguishable recombination layer which consists of mixture of an electron-injection nature child and a hole nature pouring molecule is sufficient as a recombination field, and the gestalt of a molecule pair in the junction interface of an electron-injection layer and a hole pouring layer is sufficient as it. In addition, in a recombination field, an electron-injection nature child may be a molecule which may be the same molecule as the molecule which constitutes an electron-injection layer, and is different, and a hole pouring nature child may be a molecule which may be the same molecule as the molecule which constitutes a hole pouring layer, and is different similarly.

[0035] Hereafter, a concrete material used for the organic EL element of invention of this application 1st is explained. First, the luminescence wavelength of exciplex can be designed the optimal in both the carrier-injections property (EV), i.e., the valence-band level of a recombination field, and conduction band level (EC), and a row by choosing a suitable electron-injection nature child (A) and a hole pouring nature child (D). Moreover, it is both carrier transport-properties, i.e., electron mobility, mue by both mixed ratio. Hall mobility muh It can optimize. Hereafter, the electron-injection nature child (A) and hole pouring nature child (D) who are used for this invention are illustrated more concretely.

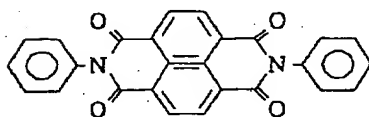
[0036] The difference (EC) from the vacuum level of the conduction band level in the band structure formed in the strong order, i.e., the thin film state, of electron-injection nature shows an electron-injection nature child below to descending. These Pentacene Dacron (A1), diphenyl NAFUTARENTETORA KARUBOKISHIIMIDO (A2), The alloxazine (A3), perylene tetrapod carboxy imide (A4), p-vinyl cyano alkyl ester (A5) SHIANUIKKU acid triphenyl imide (A6), N-phenyl naphthalene dicarboxyimide (A7), piperonal BINIRUSHIANO alkyl ester (A8), They are PY (A9), a diphenyl OKISA diazole (A10), benzoxazole (A11), diphenyloxazole (A12), and a hexa phenylbenzene (A13).

[0037]

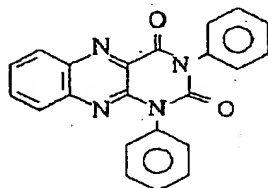
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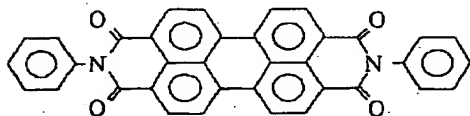
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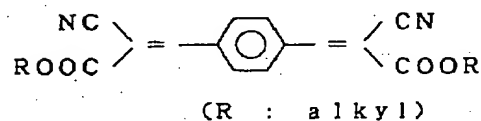
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(A3)



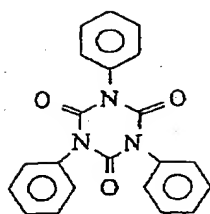
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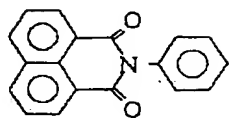
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[0038]

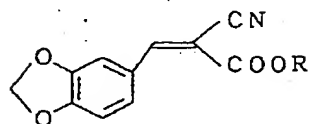
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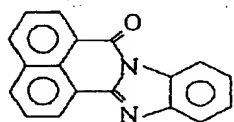


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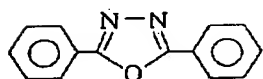


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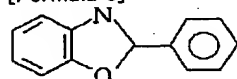
(R : alkyl)



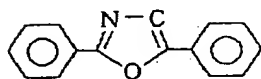
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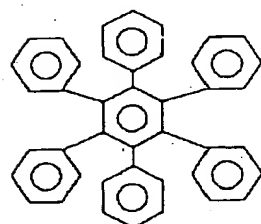
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[0039]
[Formula 6]

(A11)



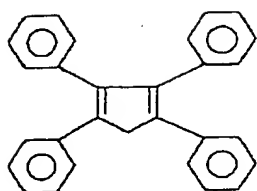
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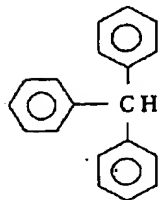
(A13)

[0040] The difference (eV) from the vacuum level of the valence-band level in the band structure formed in the weak order, i.e., the thin film state, of hole pouring nature shows a hole pouring nature child below to descending. These are TPCP (D1), a triphenylmethane color (D2), a tetrapod phenylethylene (D3), a triphenylamine (D4), dialkyl phenylamine (D5), and a Quinacridone (D6).

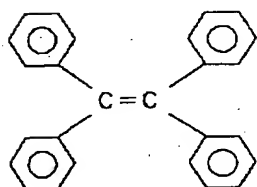
[0041]
[Formula 7]



(D 1)

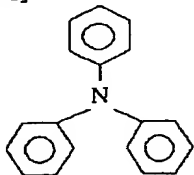


(D 2)

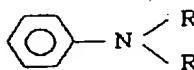


(D 3)

[0042]
[Formula 8]

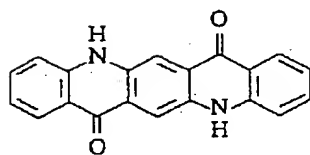


(D 4)



(D 5)

(R : a l k y l)



(D 6)

[0043] Although only the fundamental skeleton was illustrated above, what combined two or more sorts of basic skeletons chosen from the dimer of these basic skeletons, trimers, or these basic skeletons can also be used.

[0044] Next, the mixing ratio of A and D in the recombination layer which consists of mixture of an electron-injection nature child (A) and a hole pouring nature child (D) is explained. By this mixing ratio, it is electron mobility μ_{e} . And Hall mobility μ_{H} it can control, as a result is etarec. It can improve. Generally, the electron mobility of a recombination layer and Hall mobility are designed so that it may become of the same grade as a digit. However, although there is much large material of Hall mobility, there is little large material of electron mobility. For this reason, it is μ_{H} when A and D are mixed equivalent [every]. μ_{e} It may compare and may become a value large 1-2 figures. In this case, μ_{H} μ_{e} In order to make it of the same grade, the thing which lessen mol concentration of D and for which mol concentration of D is specifically made 5 - 30% is effective.

[0045] Moreover, it is μ_{H} μ_{e} , maintaining the range same as a digit by designing the combination and element structure of D and A suitably, in order to raise efficiency. μ_{H} μ_{e} It can also tune finely so that it may become. For example, the strength of the electron-injection nature of a recombination layer compares with the strength of hole pouring nature, and when weak (i.e., EMe-EC), it is. (A) $>E_{MH}-E_{V}$ The hole injection rate to a recombination layer increases compared with the amount of electron injections at the time of (D). In this case, μ_{H} μ_{e} It is effective to set up and to lengthen residence time of the hole in the recombination layer at the time of element operation. Similarly, the strength of the hole pouring nature of a recombination layer compares with the strength of electron-injection nature, and when weak (i.e., EMe-EC), it is. (A) $>E_{MH}-E_{V}$ The amount of

electron injections in a recombination layer increases compared with hole injection rate at the time of (D). In this case, $\mu_{\text{h}} > \mu_{\text{e}}$ it is effective to carry out and to lengthen residence time of the electron in the recombination layer at the time of element operation.

[0046] Moreover, it is μ_{e} when the junction state between organic thin films is disadvantageous for a carrier shutting up. And μ_{h} By adjusting, a carrier closes and eye ** can be realized. Specifically, D and A are distributed in polymer and it is μ_{h} . And μ_{e} Both are made small. Thus, μ_{e} in a carrier-injection layer and μ_{h} It compares and they are μ_{e} of a recombination layer, and μ_{h} . It can be made small. However, as for the sum [as opposed to polymer in this case] of the content of D and A, it is desirable that it is more than 10mol%. As polymer which can be used, there are polystyrene, poly (p-t-butyl styrene), poly (vinylcarbazole), poly (vinyltoluene), poly (methyl methacrylate), the poly (acrylonitrile) copolymer, poly (vinyl acetate) and a condensation polymer, for example, polyester, a polycarbonate, a polyimide, a polysulfone, etc. Moreover, if D and A are distributed into polymer by predetermined variance in a carrier-injection layer, the same control as the time of adjusting the mixing ratio of A and D in a recombination layer also about the case where a molecule pair is formed by the junction interface of an electron-injection layer and a hole pouring layer, and it becomes a recombination field, as mentioned above can be performed.

[0047] In this application the 1st invention, when exciplex luminescence arises temporarily, combination of A and D from which the luminescence wavelength of short wavelength is obtained from desired luminescence wavelength is chosen. Hereafter, the exciplex luminescence wavelength obtained in the combination of an electron-injection nature child (A) and a hole pouring nature child (D) is illustrated to Table 1.

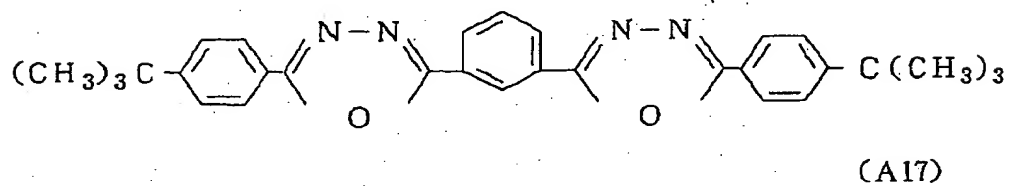
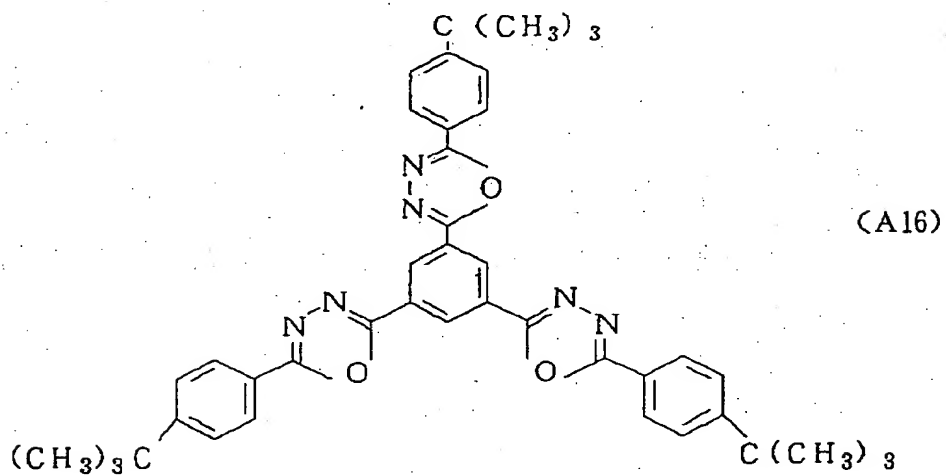
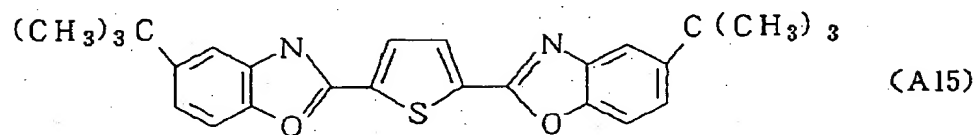
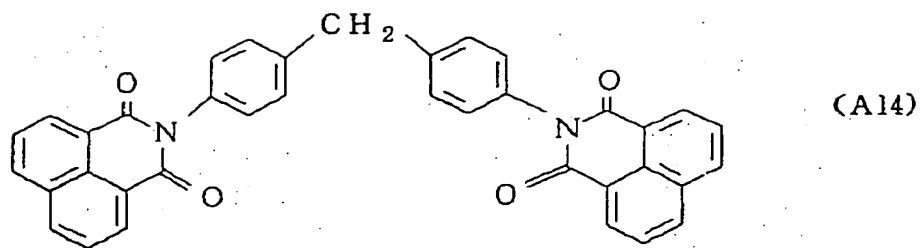
[0048]

[Table 1]

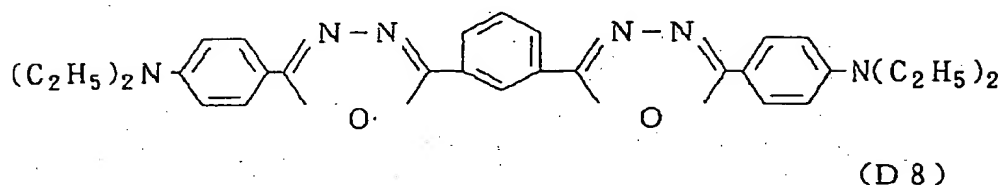
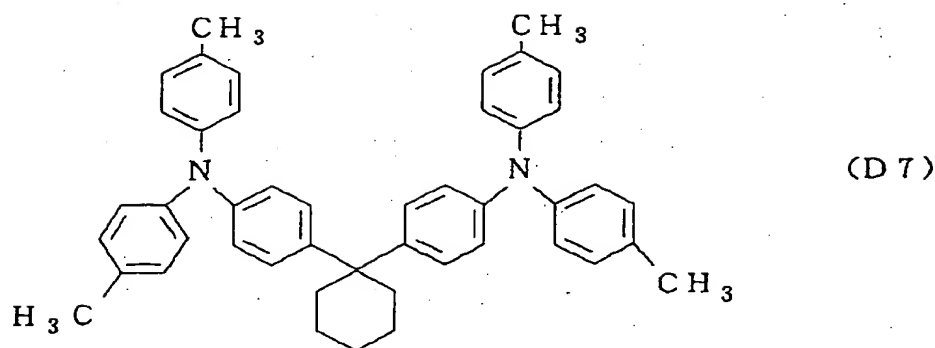
A	D	エキサイプレックス 発光波長ピーク (nm)	発光色
DNIBPC (A14)	ジアミン (D7)	616	橙
DNIBPC (A14)	OXD-8 (D8)	580	黄
BBOT (A15)	ジアミン (D7)	540	緑
BBOT (A15)	OXD-8 (D8)	532	緑
OXD-S1 (A16)	ジアミン (D7)	499	緑
OXD-S1 (A16)	OXD-8 (D8)	483	青緑
OXD-7 (A17)	ジアミン (D7)	460	青

[0049]

[Formula 9]



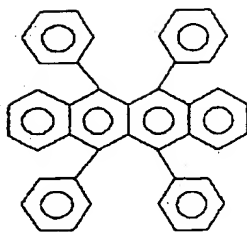
[0050]
[Formula 10]



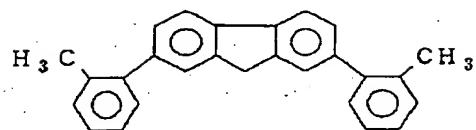
[0051] In this application the 1st invention, what has high etaPL is chosen in the state of an isolated state (thin state) or a microcrystal as a molecule used as a luminescence site. The luminescent molecule which has etaPL specifically higher than etaPL of the exciplex generated in a recombination field is used, and it is desirable that etaPL in an isolated state or a microcrystal state is 20% or more and 50 more% or more. As such a molecule, there are a molecule of an aromatic system as shown in "izing 11" - "izing 16", a molecule for scintillators, laser coloring matter, etc. Namely, rubrene (L1), a fluorene derivative (L2), a perylene (L3), 9, 10-dimethyl anthracene (L4), 9, 10-screw (phenyl ethynyl) anthracene (L5), 2, 5-diphenyl furan (PPF, L6), the 2, 5-diphenyloxazole (PPO, L7), A 2-(1-naphthyl)-5-phenyl oxazole (an alpha-NPO, L8), 2-(4-biphenyl) oxazole (BPO, L9), 2, 5-G (4-biphenyl) oxazole (BBO, L10), 2, 5-diphenyl - 1, 3, 4-OKISA diazole (purified protein derivative, L11), 2-(1-naphthyl)-5-phenyl - 1, 3, 4-OKISA diazole (alpha-NPD, L12), 2-(2-naphthyl)-5-phenyl - 1, 3, 4-OKISA diazole (beta-NPD, L13), 2-phenyl-5-(4-biphenyl)- 1, 3, and 4-OKISA diazole (PBD, L14) -- 2, 5-G (4-biphenyl) - 1, 3, 4-OKISA diazole (BBD, L15), 2, 5-G (1-naphthyl) - 1, 3, 4-OKISA diazole (alpha-NND, L16), 2, 5-G (2-naphthyl) - 1, 3, 4-OKISA diazole (beta-NND, L17), 1, 4-screw-[2-(5-phenyl oxazolyl)] benzene (POPOP, L18), 1, 4-screw-[2-(4-methyl-5-phenyl oxazolyl)] benzene (Dimethyl POPOP, L19), Screw-(isopropyl styryl) benzene (BPSB, L20), 2, a 5-screw-[5-t-butyl benzoxazolyl (2)] thiophene (BBOT, L21), A diphenyl stilbene (DPS, L22), p-terphenyl (L23), A hexa phenyl (L24), pen terphenyl (L25), a dialkoxy polyphenyl (L26), A 9-amino acridone (L27), Rhodamine B (L28), 9, 10-diphenyl anthracene (L29), an acridone (L30), oxazine (L31), DCM (L32), etc. are mentioned.

[0052]

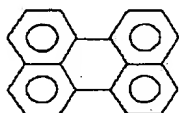
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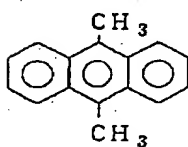
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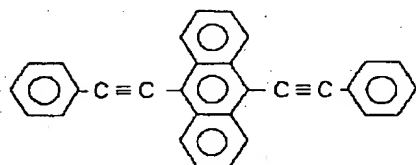
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(L 3)



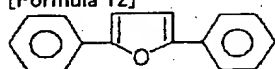
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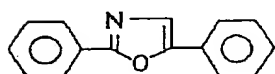
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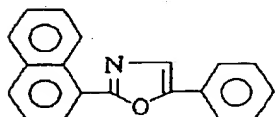
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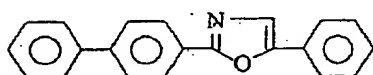
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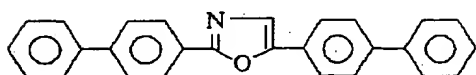
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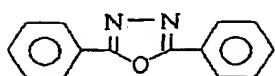
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(L 9)



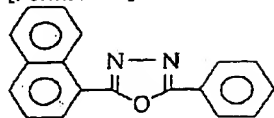
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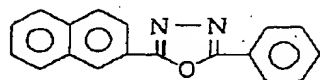
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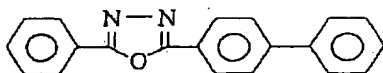
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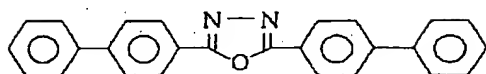
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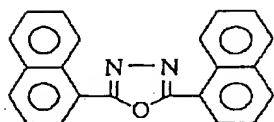
(L13)



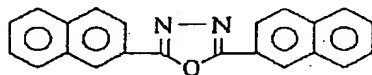
(L14)



(L15)



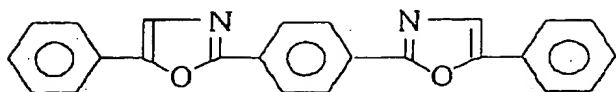
(L16)



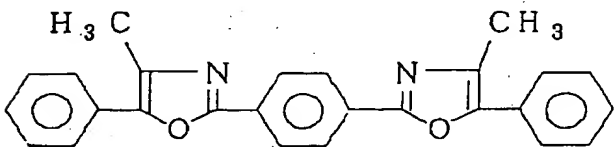
(L17)

[0055]

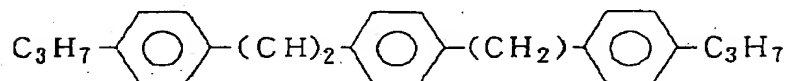
[Formula 14]



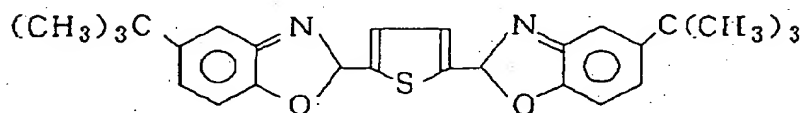
(L18)



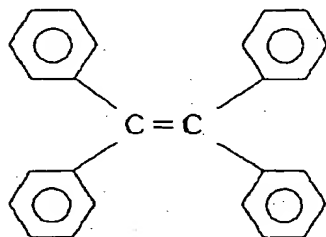
(L19)



(L20)

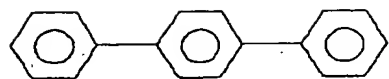


(L21)

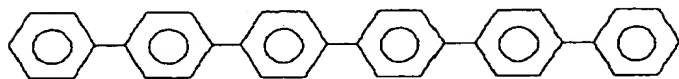


(L22)

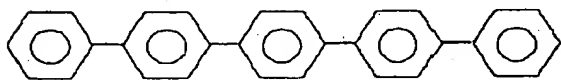
[0056]
[Formula 15]



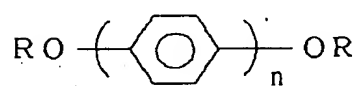
(L23)



(L24)

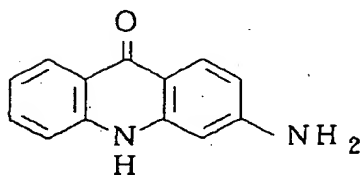


(L25)

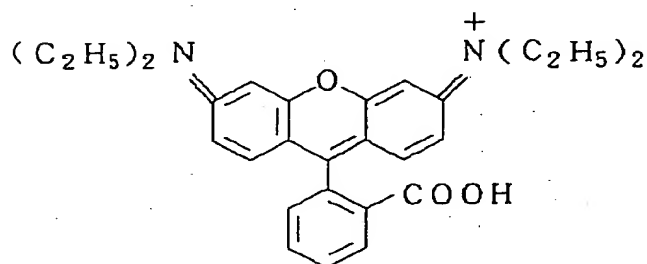


(L26)

$n = 3 \sim 6$ R : アルキル基

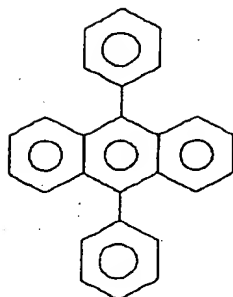


(L27)

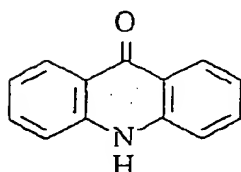


(L28)

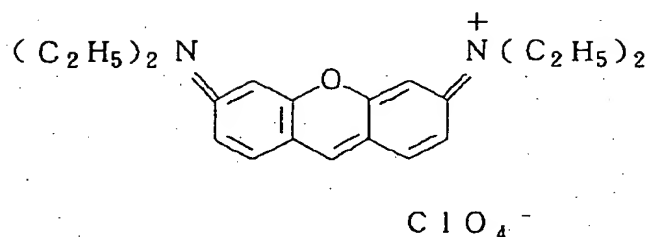
[0057]
[Formula 16]



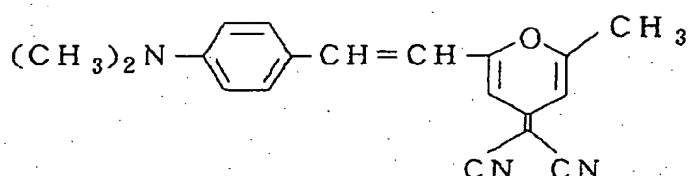
(L29)



(L30)



(L31)



(L32)

[0058] As for a luminescent molecule, it is desirable to choose with careful attention to luminescence wavelength, a carrier-injection property, and polarity. In order to obtain desired luminescence wavelength, the luminescent molecule which has an optical band gap smaller than the energy of the exciplex in a recombination field is chosen. When a surrounding molecule (henceforth a host) differs in a property greatly from a luminescence site about a pouring property, exciplex luminescence between a host and a luminescence site arises, and there is a possibility that it may become impossible to employ efficiently high etaPL which a luminescence site originally has. In order to avoid this, when setting conduction band level of EV (Host), EV (dop), a host, and a luminescence site (dopant) to EC (Host) and EC (dop) for the valence-band level of a host and a luminescence site (dopant), respectively, the $\text{EV(dop)}-\text{EV (Host)} < 0.6\text{eV}$ and $\text{EC (Host)}-\text{EC(dop)} < 0.6\text{eV}$ thing fulfilled for one of relations at least is desirable. Moreover, in order to avoid exciplex luminescence between the layer containing a luminescence site, and the adjoining layer, it is more desirable than these interfaces not to dope a luminescent molecule within 0.5nm. Furthermore, in like, when mutually approximated about the polarity of a host and a luminescence site, since etaPL becomes high, it is desirable. This is because a meeting of luminescence sites will be promoted if the polarity of a host and a luminescence site differs greatly.

[0089]

[Example] Hereafter, the example of this invention is explained.

an example 1 — the organic EL element shown in drawing 1 by the following methods was produced First, it is the sheet resistance 10 ohm/cm 2 by the sputter on the glass substrate (the Hoya Corp. make, NA40) 1 which does not contain an alkali component. 200nm (electrode for hole pouring) of ITO electrodes 2 was formed. Next, using the vacuum evaporation system, the degree of vacuum was set as 10^{-6} Torr, substrate temperature was set as the room temperature, 50nm vacuum evaporation of the diamine (hole pouring nature child) shown by (D7) was carried out at the rate of 0.1 – 0.2 nm/s, and the hole pouring layer 3 was formed. Next, the recombination layer 4 which carries out 50nm vacuum evaporation of OXD-7 (electron-injection nature child) and (L5) the screw (phenyl ethynyl) anthracene (luminescent molecule) shown shown by the diamine (hole pouring nature child) shown by (D7) and (A17) at a rate of 1:1:0.01, and contains a luminescent molecule was formed. A setup of the above-mentioned rate was performed by carrying out a temperature setup of each vacuum evaporation boat independently, and controlling an evaporation rate. Next, 50nm vacuum evaporation of the OXD-7 (electron-injection nature child) shown by (A17) was carried out at the rate of 0.1 – 0.2 nm/s, and the electron-injection layer 5 was formed. Each of these organic thin films was amorphous structures. Besides, the Mg-Ag electrode (electrode for electron injections) 6 of 100nm of thickness was formed by EB vacuum deposition.

[0092] The organic EL element of examples 2-5 was produced like the example 1 using the luminescent molecule shown in two to example 5 table 1. When voltage is impressed about these elements so that an ITO electrode may be added, they are 100 mA/cm² at 10V. Current flowed and green - red luminescence was obtained. The emission peak wavelength was in agreement with PL peak wavelength of each luminescent molecule. Moreover, 4000 - 6000 cd/m² Luminescence brightness was obtained. These results are collectively shown in Table 2.

[0093]

[Table 2]

	発光性分子	発光ピーク波長 (nm)	輝 度 (cd/m ²)
実施例2	S150 (L33)	510	4000
実施例3	ルブレン (L1)	600	6000
実施例4	DCM (L32)	700	3000
実施例5	オキサジン (L31)	700	4000